

Interfacial Processes in EES Systems Advanced Diagnostics

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Project ID# ES085

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Overview

Timeline

- PI participates in the BMR Program since 1999
- This project was recompeted in FY15 and renewed in FY16 as part of Ni-rich high-voltage cathode project.
- This project is 70% complete

Barriers Addressed

- Inadequate Li-ion battery energy and power density, and calendar/cycle lifetimes for PHV and EV applications
- High cell/electrode/interface impedance that limits power and affects system safety

Budget

- FY17 funding \$440K
- FY16 funding \$440K
- FY15 funding \$500K
- FY14 funding \$500K
- FY13 funding \$500K

Partners

- ABMR Cathode and Anode Task Groups
 - ANL, LBNL, SUNY, UP, HQ, NREL, URI, UM and UU
 - G. Chen, V. Battaglia, M. Doeff, K. Persson, V. Zorba, W. Yang, H. Bechtel, C. Martin, C. Ban, B. McCloskey
- Umicore
- Farasis Energy, Inc.

Relevance : Objectives

1. Provide critical understanding of basic principles that govern the function and operation of active materials, composite electrodes and Li-ion battery cells that is necessary for successful implementation of high energy density materials in Li-ion cells for PHEVs and EVs .
 - Establish direct correlations between electrochemical performance, interfacial phenomena, surface chemistry, morphology, topology and degradation mechanisms of ABMR baseline materials, electrodes and cells.
2. Propose and evaluate remedies to interfacial and materials instability e.g., artificial surface coatings (e.g., ALD) and/or structures, novel electrode architectures, electrolyte additives etc.
3. Develop, adapt and employ new advanced experimental techniques and methodologies to guide development of novel EES materials, electrodes and battery systems.
 - Obtain detailed insight into the dynamic behavior of molecules, atoms, and electrons at electrode/electrolyte interfaces at resolution that is adequate to the size and function of basic chemical or structural building blocks

Milestones

1. Determine relationship between surface reconstruction and aging/cycling of in NMC powders/electrodes. **Status completed** (December, 2016).
2. Complete in situ AFM characterization of interfacial activity of the model NMC material in organic carbonate electrolytes. **Status on schedule.**
3. Determine the composition of the surface film and its effect on the, electrochemical performance of NMC electrodes. **Status completed** (March 2017)
4. Determine relationship between surface reconstruction, film formation and metal dissolution in NMC electrodes. Go/No-Go Criteria: Consider development of effective remedies to interfacial degradation of NMC electrodes. **Status on schedule.**

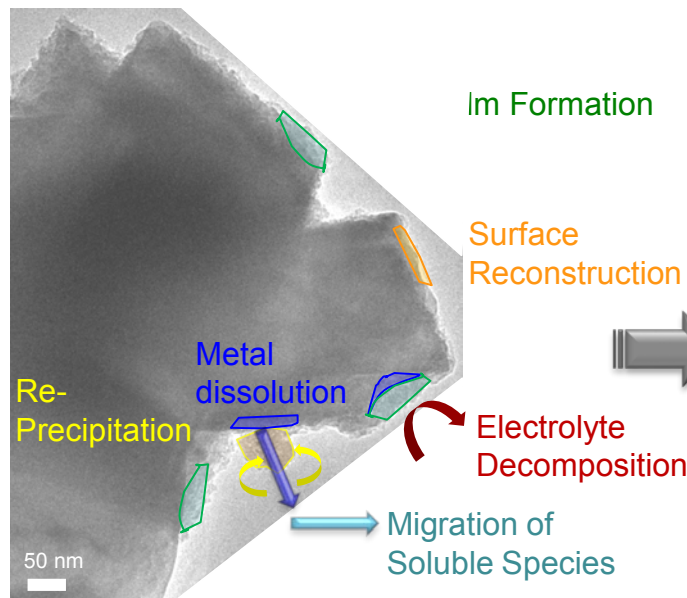
Interfacial Reactivity of Ni-rich NMC Cathodes

Approach

Develop, apply and couple advanced characterization techniques, such as optical (Raman, FTIR, ellipsometry), X-ray (XAS, XPS, XANES), electron (SEM, EELS, TEM) and scanning probe spectroscopy and microscopy with standard electrochemical methods to determine function, operation and degradation of materials, electrodes and battery cells.

1. Study interfacial reactions between organic electrolytes and Ni-rich NMC.
2. Investigate the impact of surface reconstruction layer(s) on the electrochemical behavior of the NMC cathode.
3. Obtain detailed insights into the mechanism and interdependence of interfacial phenomena at Ni-rich NMC cathodes.

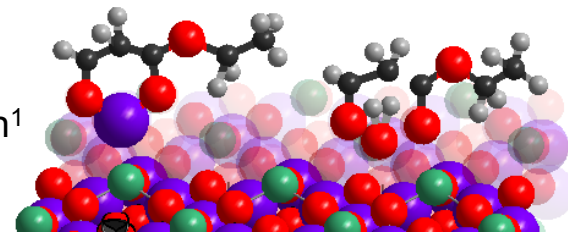
Interfacial Reactivity of Ni-rich NMC Cathodes



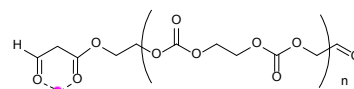
Adapted from J. Vetter, et al., *J. Power Sources*, 2005, **147**, 269-281

1. Electrolyte Decomposition¹

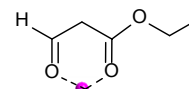
2. Metal Dissolution¹



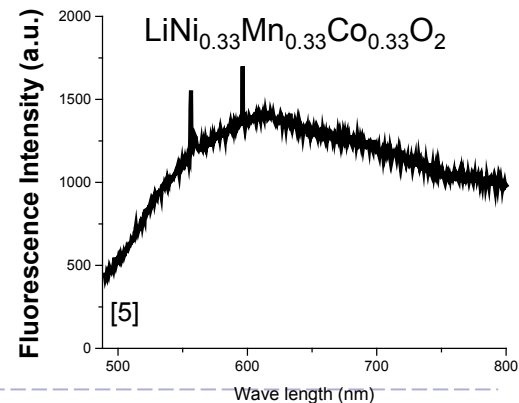
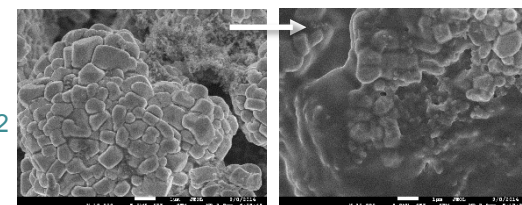
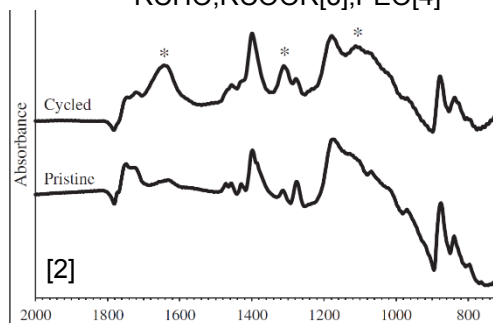
3. Fluorescent Surface Film Formation¹⁻⁵



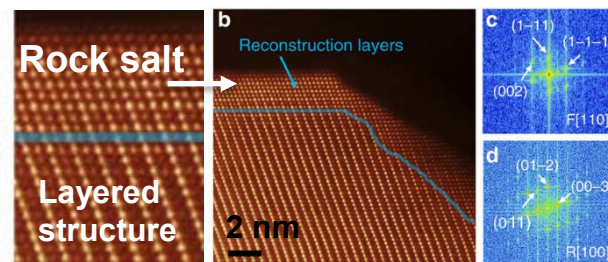
4. Migration of Soluble Species^{1,2}



* Carbonyl groups:
RCHO, RCOOR[3], PEO[4]



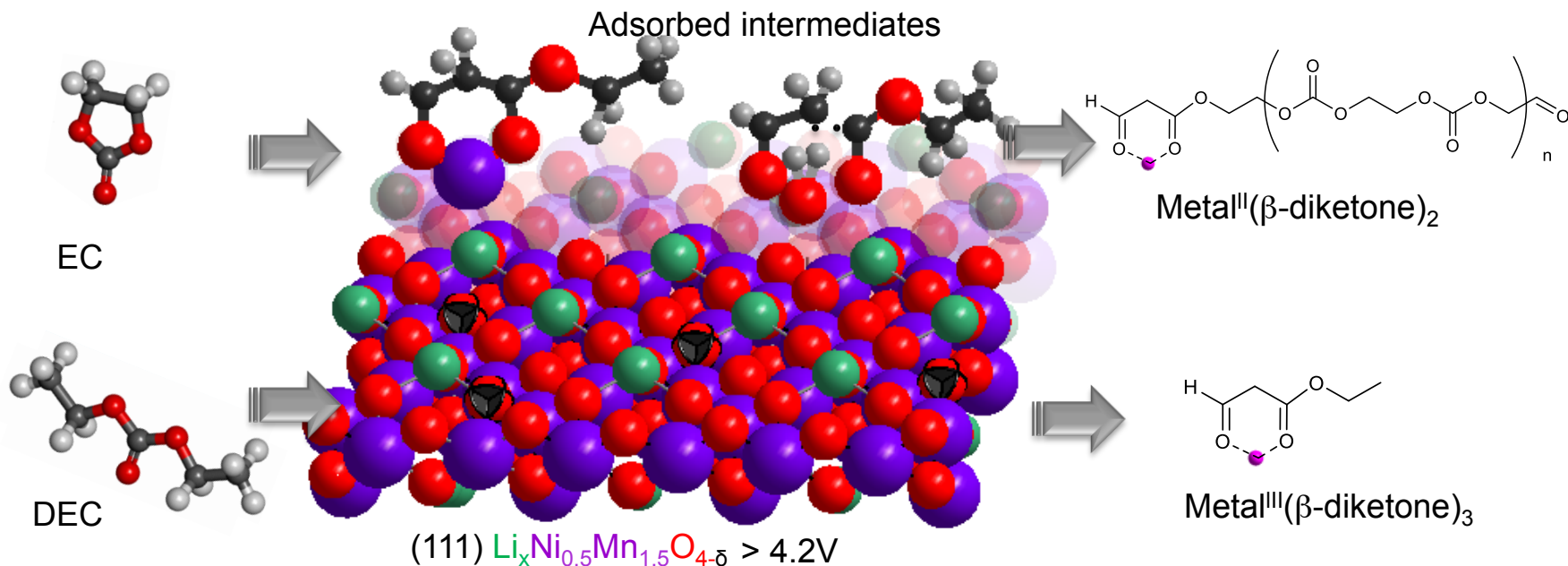
5. Surface reconstruction⁶



1. A. Jarry et al., *JACS*, **137**, 3533-3539, (2015).
2. N. S. Norberg et al., *Electrochem. Commun.* **34**, 29-32, (2013)
3. M. Moshkovich et al., *J. Electroanal. Chem.*, **497**, 84, (2001)
4. S. E. Sloop et al., *J. Power Sources*, **119-121**, 330-337, (2003)
5. 2016 AMR report
6. Lin et al., *Nat. Com.*, (2014)

Surface Reactivity of High-Voltage Cathodes

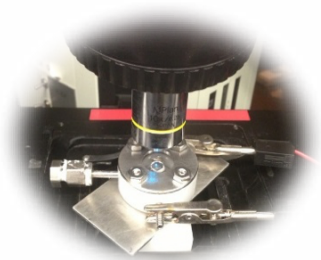
Solvent oxidation at transition metal oxide surface is enhanced by surface oxygen vacancies and results in metal dissolution via the formation of fluorescent Metal(β -diketone) complexes.



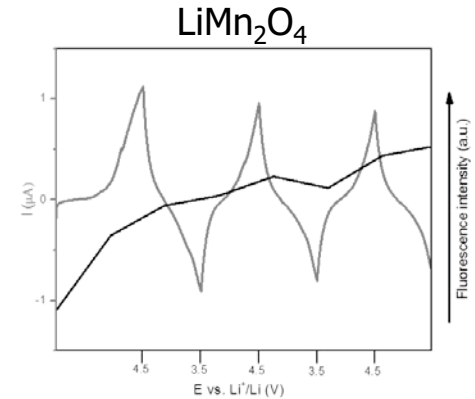
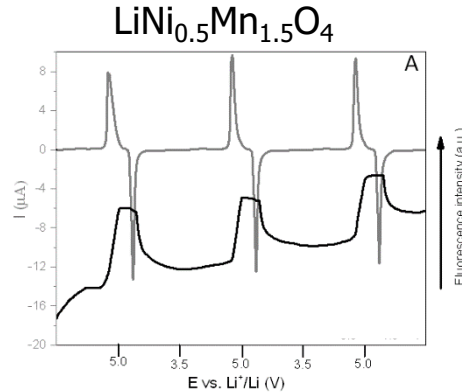
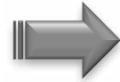
- Oxidation of EC and DEC leads to formation of Metal(β -diketone) fluorescence complexes. Polymer side-chain propagation occurs during EC decomposition.
 - EC oxidation produces high molecular weight Metal^{III}(β -diketone) complexes which contribute to the build-up of a surface film at the cathode surface.
 - DEC oxidation leads to formation of Metal^{III}(β -diketone) fluorescent complexes with short side chains which dissolve in the electrolyte.
- These mechanisms of metal dissolution are both enhanced by the continuous creation of oxygen vacancies which will most likely result in surface reconstruction processes.

Metal Dissolution/Fluorescence Complex Formation at Transition Metal Oxide Cathodes

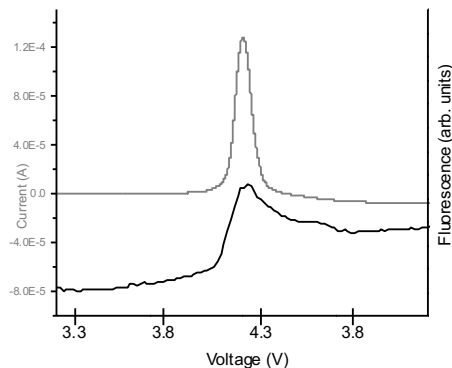
1 mol L⁻¹ LiPF₆ in EC/DEC (1/2 weight ratio)



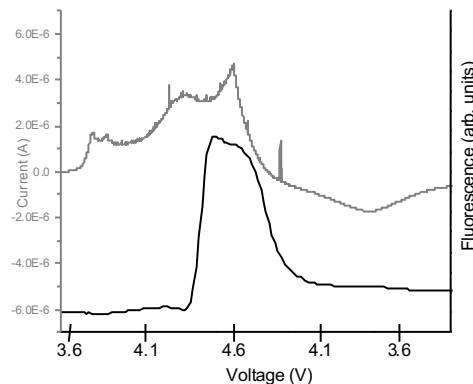
Powder pressed into Al foil as working electrode



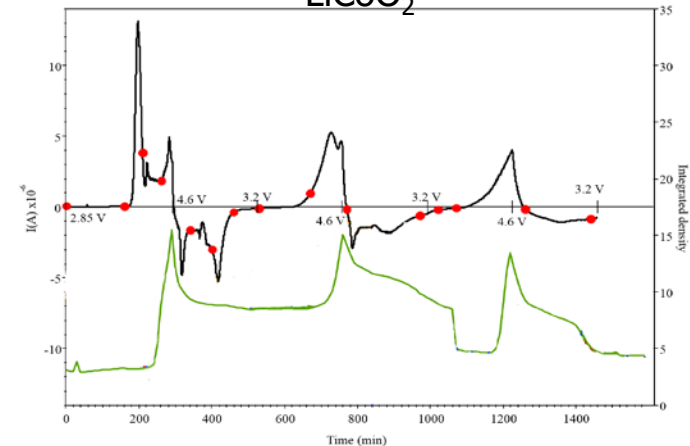
LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ (NMC)



Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O₂

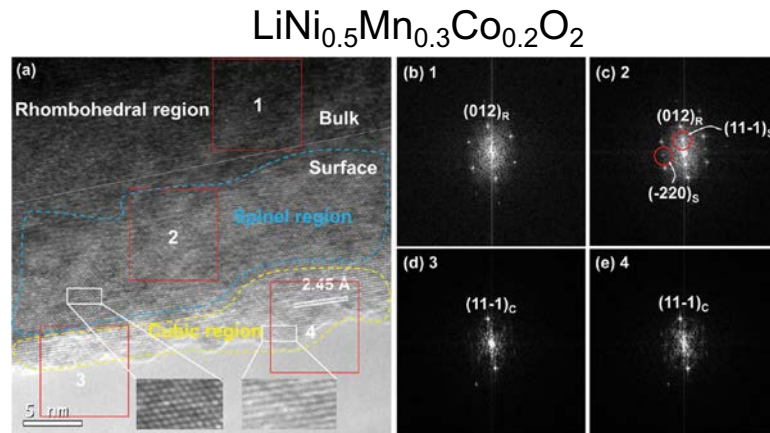


LiCoO₂

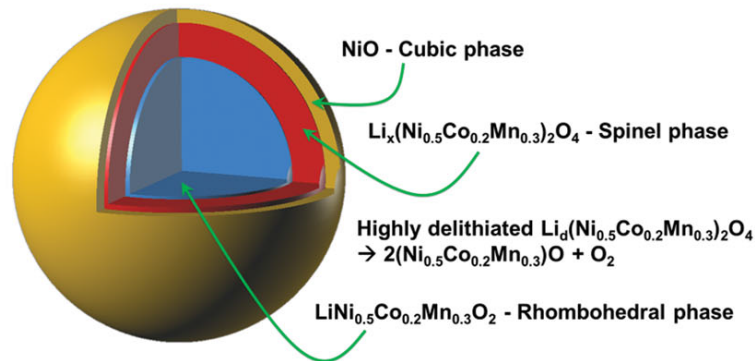


- Formation of soluble and insoluble fluorescent species is a common phenomenon observed at all transition metal oxide surface during cycling at high potentials.
 - It coincides with Li⁺ deintercalation and originates from solvents oxidation and metal dissolution.

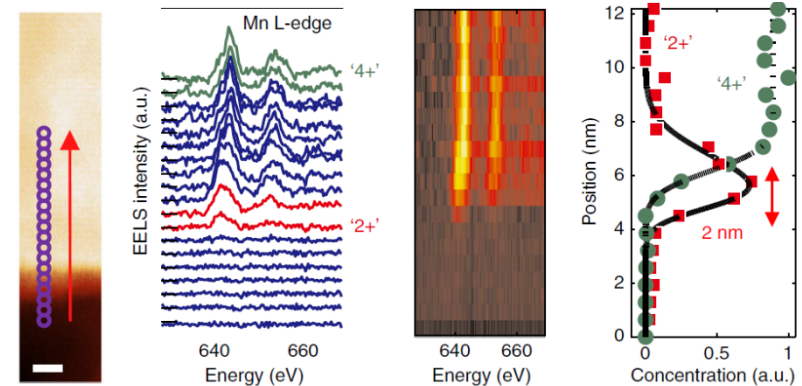
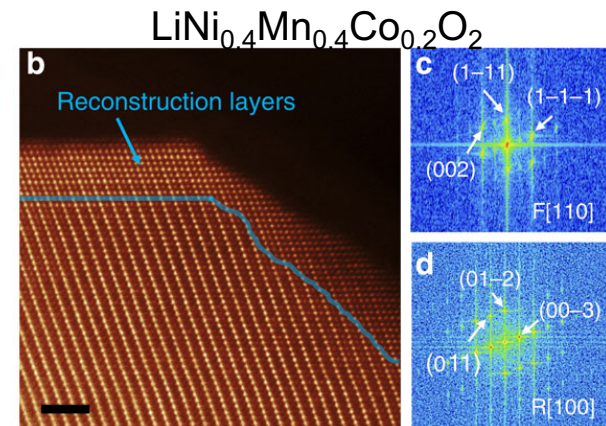
Surface Reconstruction in Ni-rich NMC Cathodes



After cycling at 3-4.8V



Jung SK, et al., Adv. Energy Mater 4, (2014).



Lin et al., Nat. Commun., (2014)

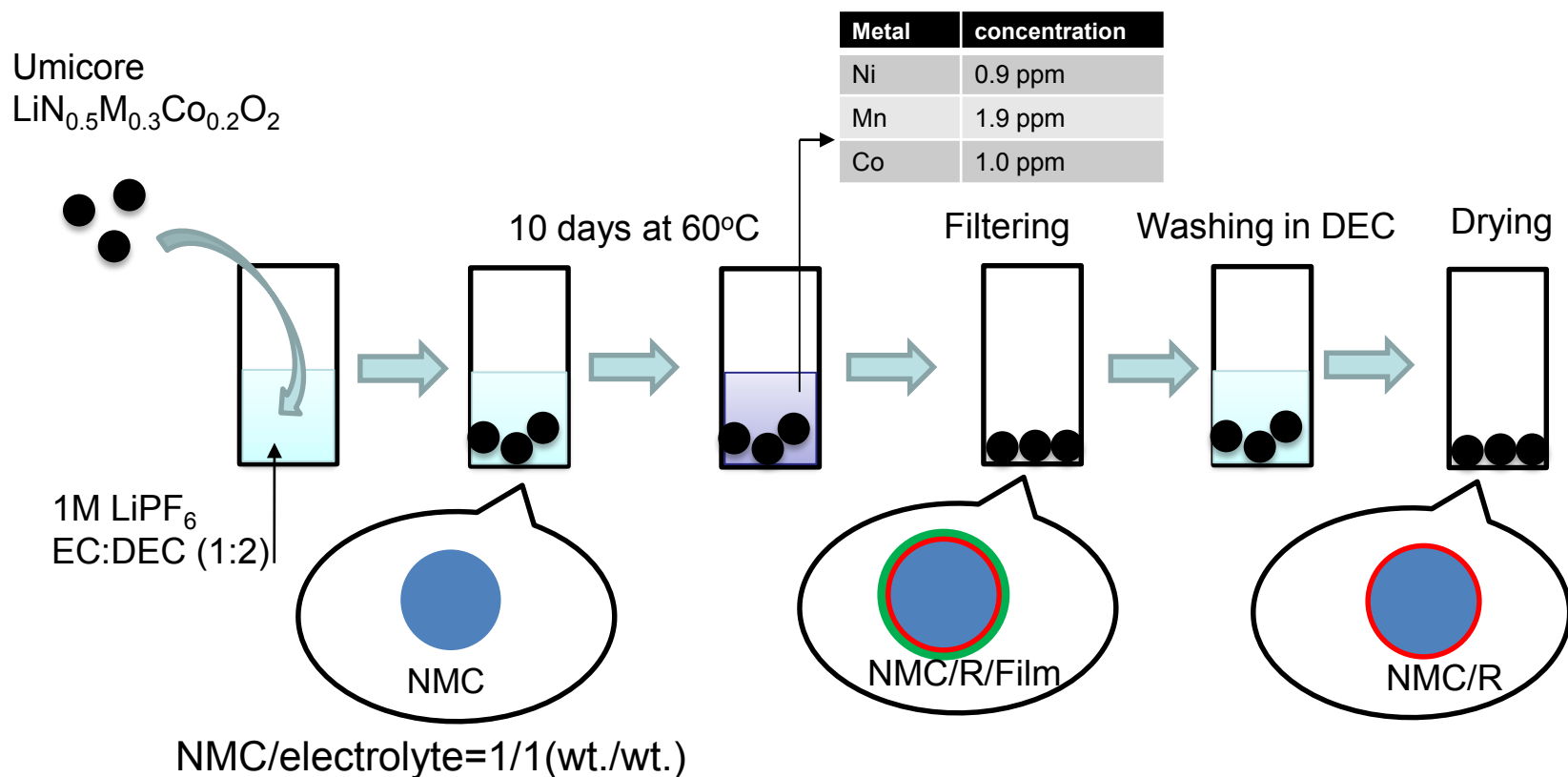
Surface reconstruction at transition metal oxide surfaces i.e., layered-spinel-rock salt structure transformation and transition metal reduction, is a common surface degradation processes in Li-ion cathode oxide materials.

Does the surface reconstruction layer impact the electrode and battery rate performance and cycle life?

The Effect of Surface Reconstruction in NMCs Materials

Experimental Approach

1. Artificially induce surface transformation of the NMC into layered-spinel-rock salt structure
2. Evaluate electrochemical properties of the surface modified NMC material

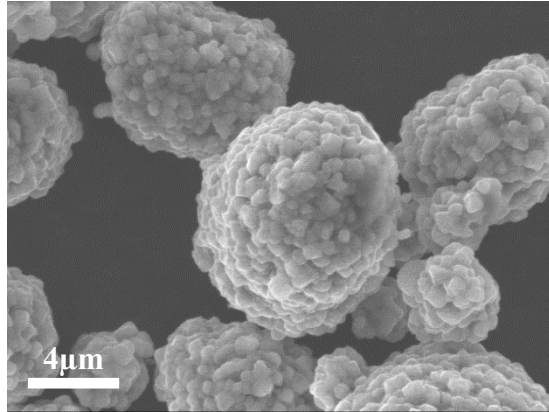


The Effect of Surface Reconstruction in NMCs Materials

Pristine NMC



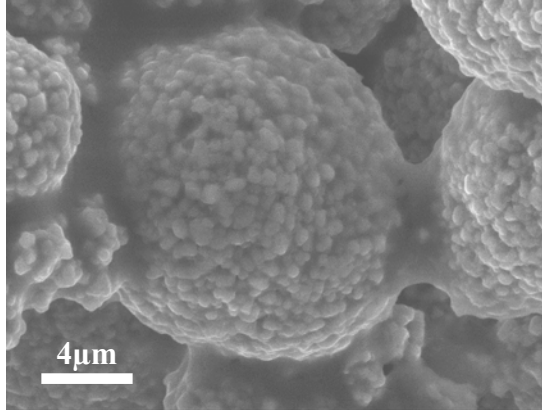
NMC



NMC a
to electrolyte



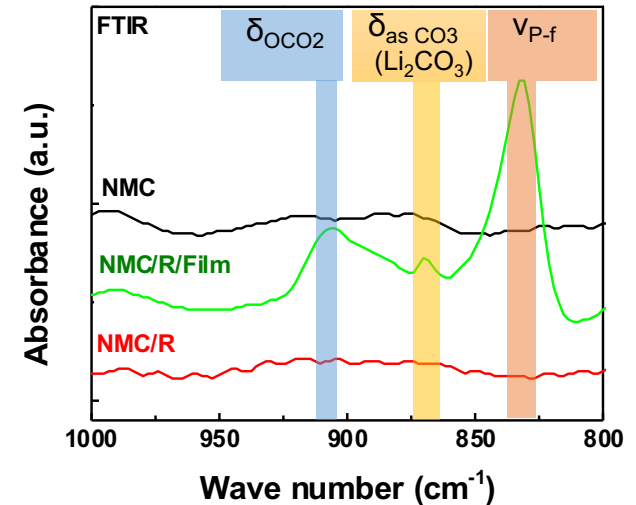
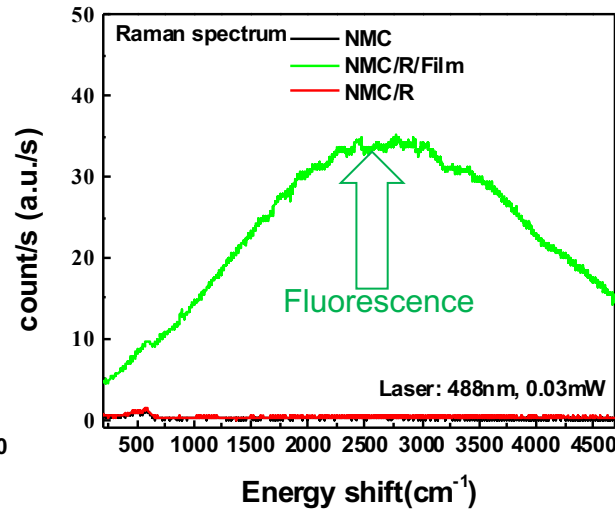
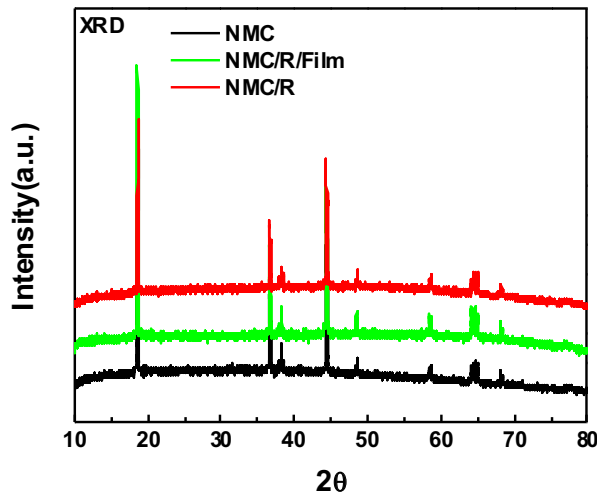
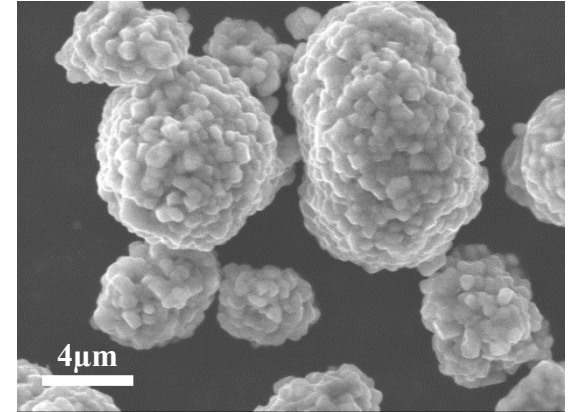
NMC/R/Film



NMC after exposure to
electrolyte + washing



NMC/R

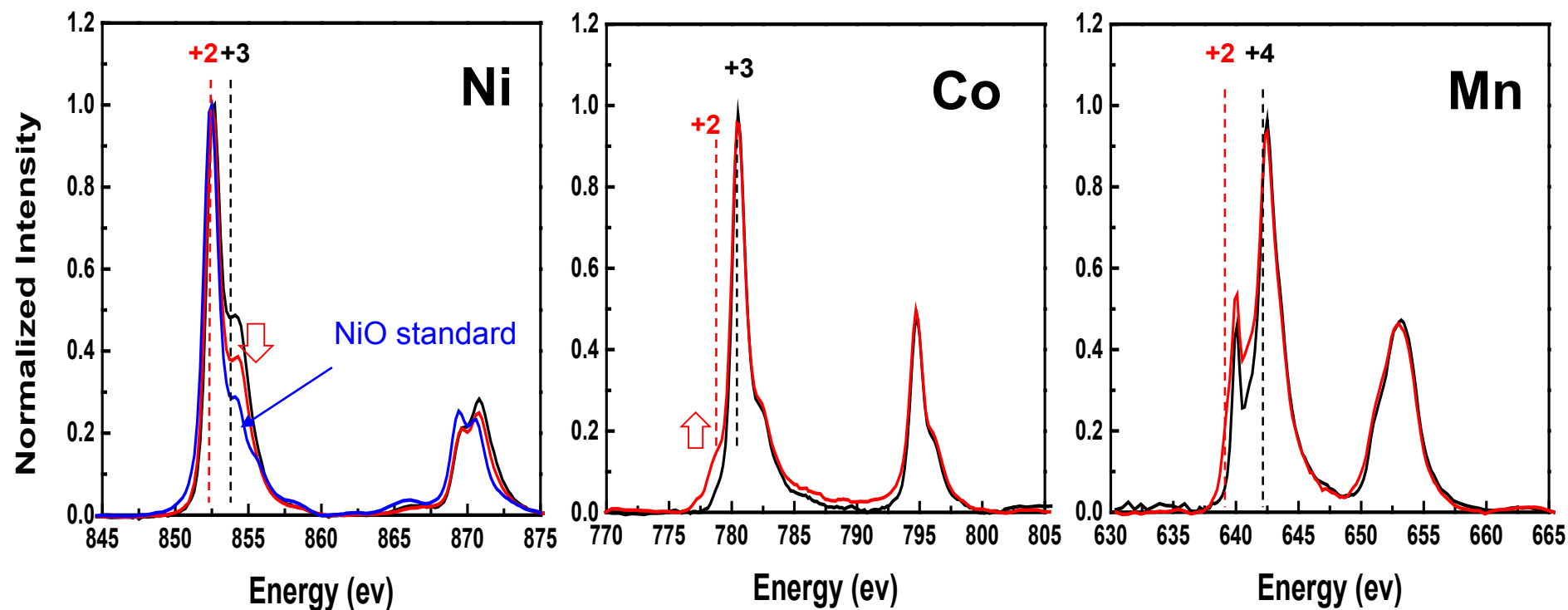


- NMC bulk structure remains intact after ageing in the electrolyte at 60°C
- Strong fluorescence emission from aged NMC
- FTIR spectral evidence of organic and inorganic electrolyte decomposition products
- Surface film can be removed by washing in DMC

Ageing of NMC in electrolyte at 60°C leads to electrolyte decomposition and surface film formation

The Effect of Surface Reconstruction in NMCs Materials

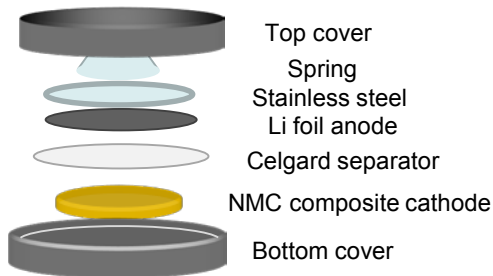
X-ray absorption spectroscopy in TEY mode:
chemical information from 5nm depth



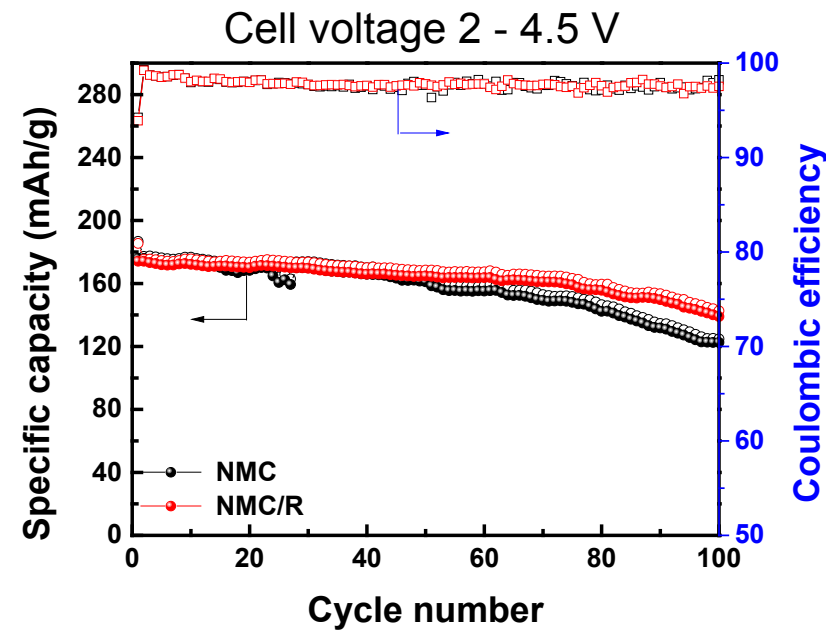
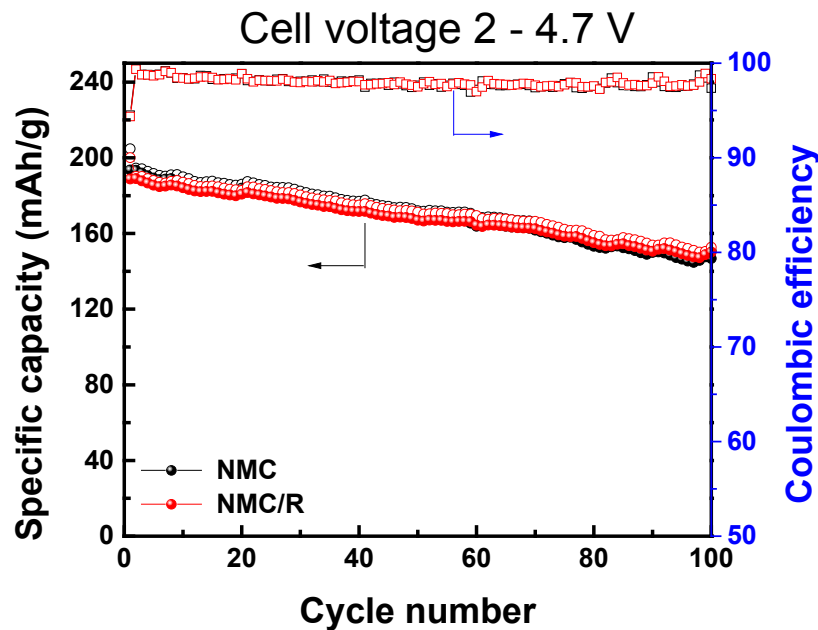
X-ray absorption spectra provide a direct evidence of formation of the surface reconstruction layer during ageing in the electrolyte at 60°C

The Effect of Surface Reconstruction in NMCs Materials

Electrochemical Testing



- Cathode: 92.8%, $\text{LiN}_{0.5}\text{M}_{0.3}\text{Co}_{0.2}\text{O}_2$, 3.2% Carbon Black, 4% PVdF
- Electrolyte: 1 M LiPF_6 , EC:DMC (1:2 vol.)
- Cycled at C/2 (100mA/g)

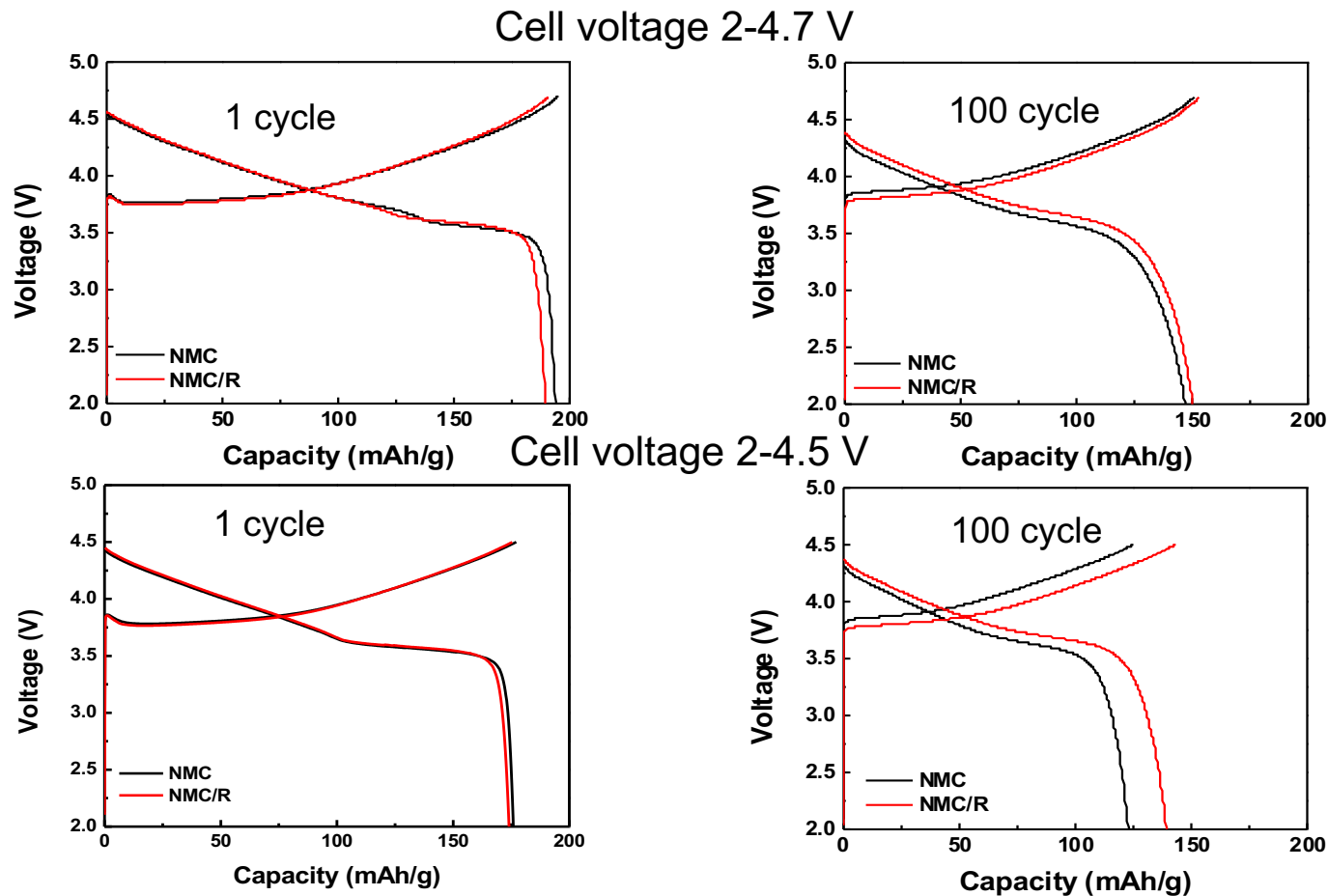


Pristine NMC and NMC/R cells exhibit similar capacity retention during cycling between 2 - 4.7 V
NMC/R shows better capacity retention during cycling between 2 - 4.5 V

The presence of surface reconstruction layer does not appear to negatively impact the electrochemical performance of the cell

The Effect of Surface Reconstruction in NMCs Materials

Electrochemical Testing



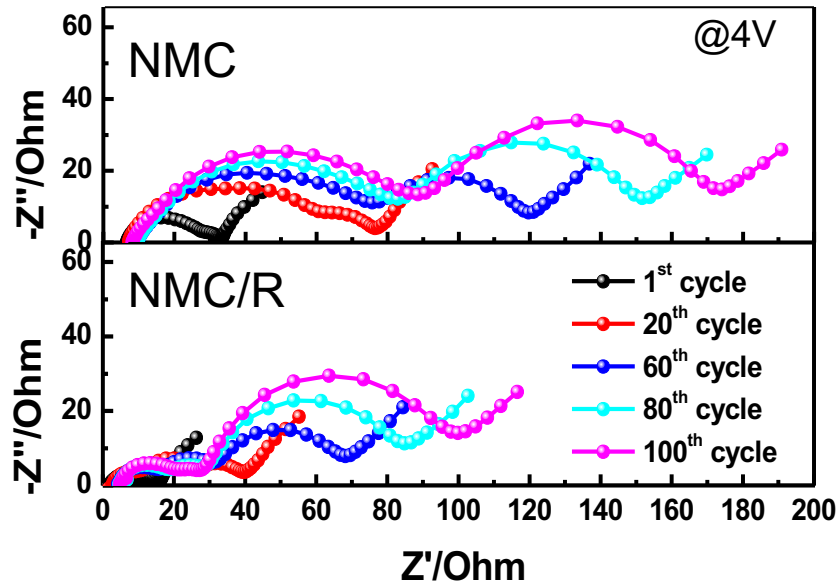
- NMC and NMC/R cells show similar polarization at the beginning of cycling
- NMC/R cell exhibits lower polarization than pristine NMC after 100 cycles

The artificially induced surface reconstruction layer appears to enhance the electrochemical performance of the cell

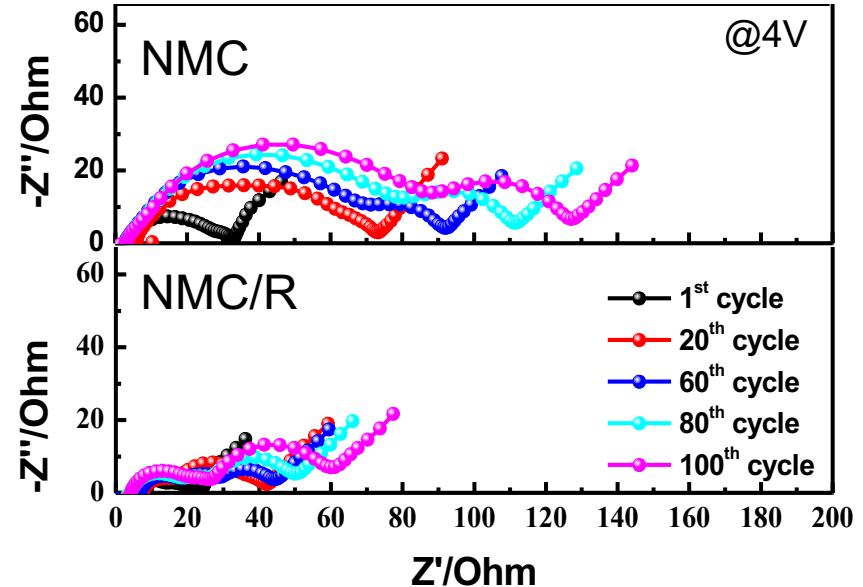
The Effect of Surface Reconstruction in NMCs Materials

Electrochemical Impedance Spectroscopy

Cell voltage 2 - 4.7 V



Cell voltage 2 - 4.5 V

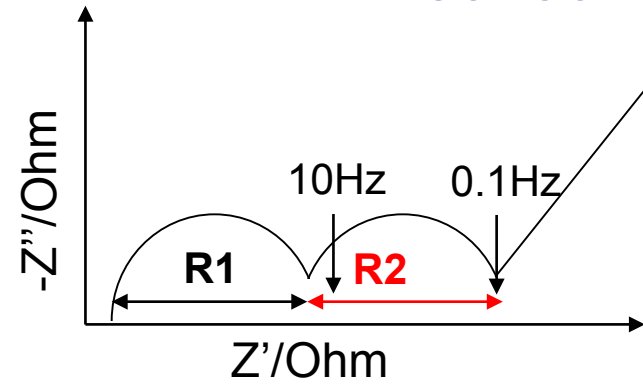


- NMC/R cells display significantly lower impedance after 100 cycles
- Cycling at higher voltages (2 - 4.7 V) results in bigger impedance increase after 100 cycles
- Electron and ion percolation phenomena in the composite electrode are mainly responsible for the observed impedance rise and capacity loss

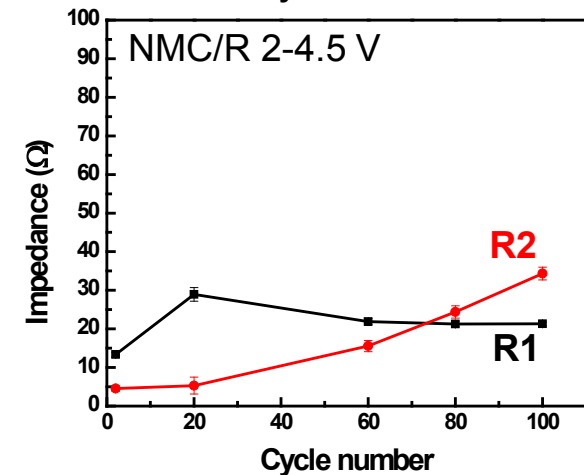
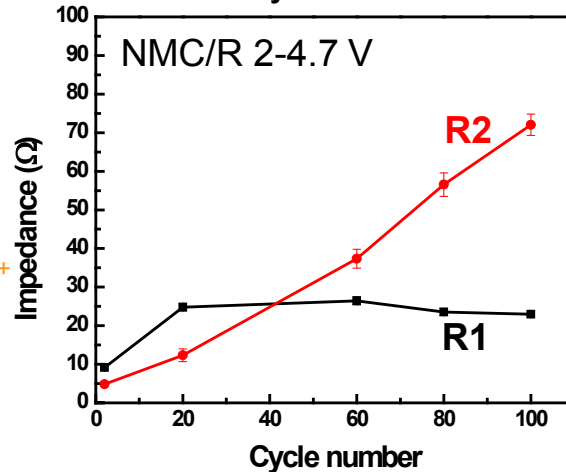
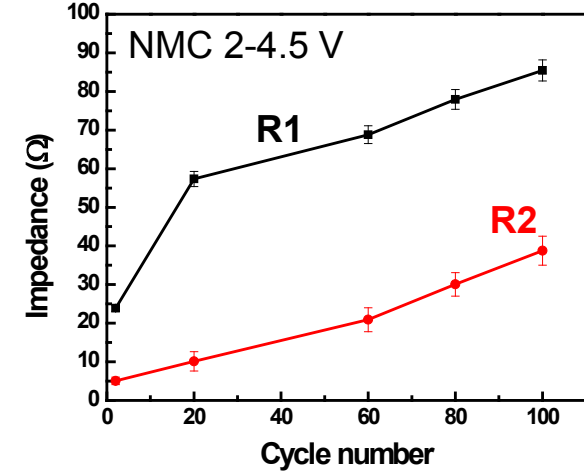
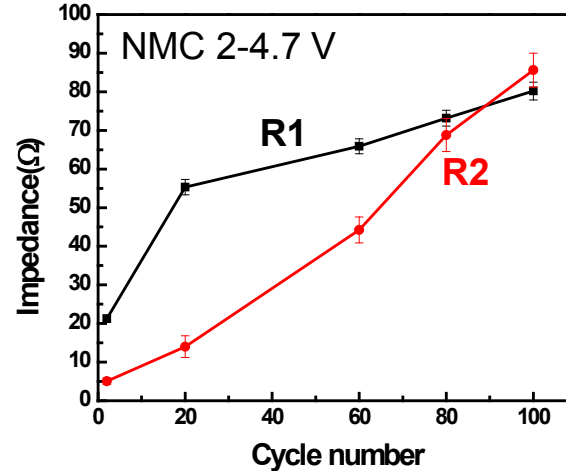
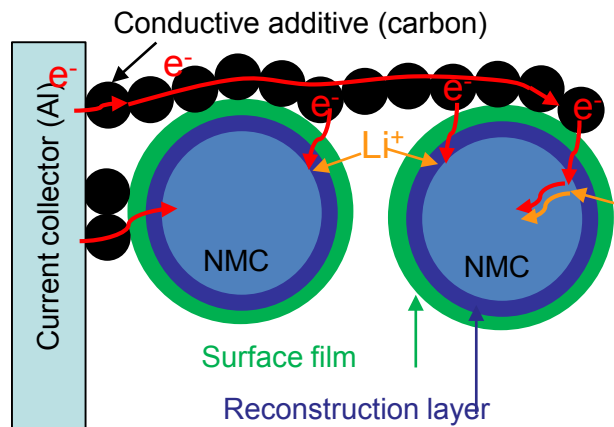
The artificially induced surface reconstruction layer appears to inhibit impedance rise during cycling of the NMC cathode

The Effect of Surface Reconstruction in NMCs Materials

Electrochemical Impedance Spectroscopy



Kerlau et al., *Electrochimica Acta*, 52 (2007) 5422
 Abarbanel et al., *J. Electrochem. Soc.* 2016, 163, A522

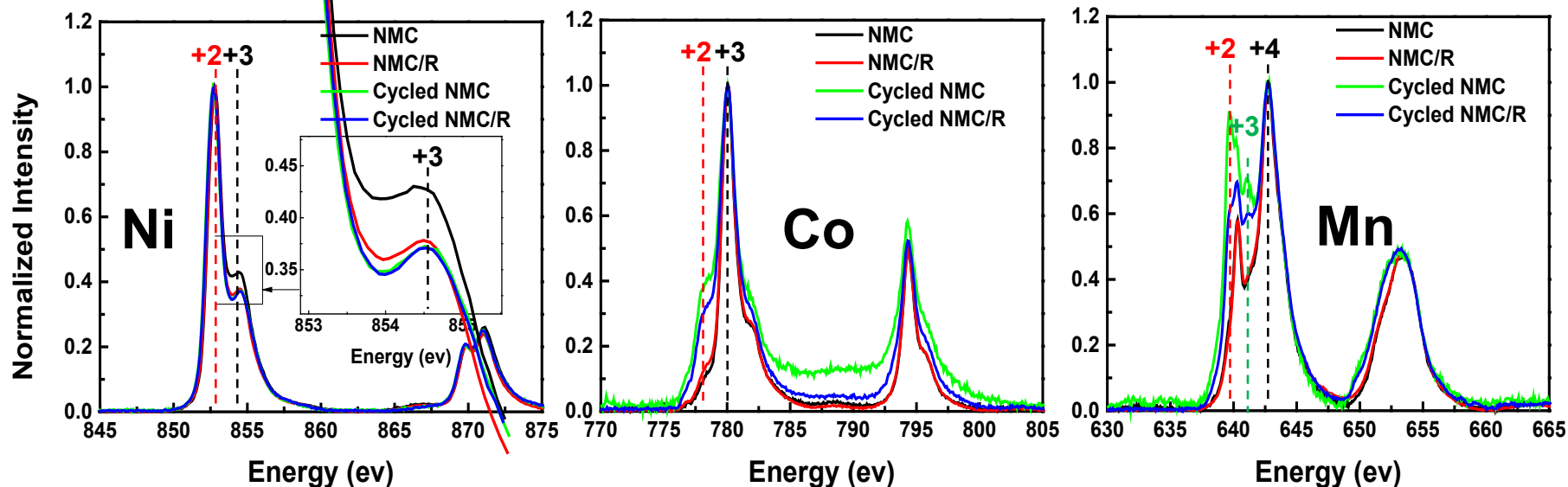
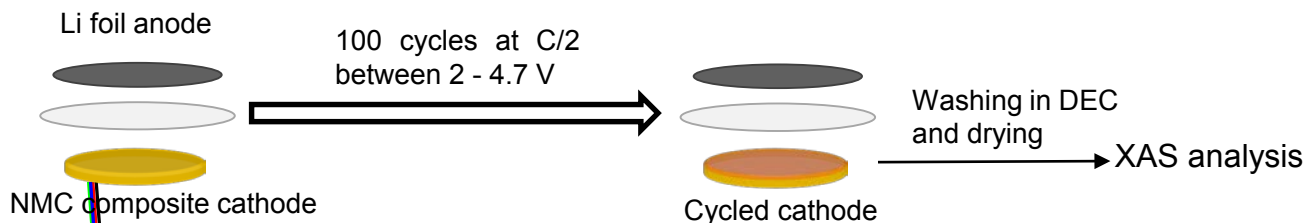


- R1 is likely related to the resistance of the surface film on cathode or the SEI on Li anode
- R2 increases during cycling at high voltage (4.7 V). Loss of electronic conductivity in the composite cathode (surface film formation, cracking of NMC secondary particles)

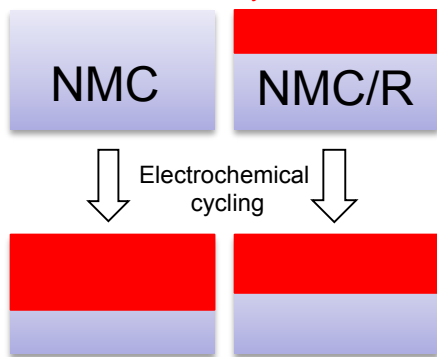
The artificially induced surface reconstruction layer may inhibit formation of surface film and Me dissolution during cycling of the NMC cathode

The Effect of Surface Reconstruction in NMCs Materials

XAS-TEY Mode of Cycled NMC Cathodes



Artificial reconstruction layer

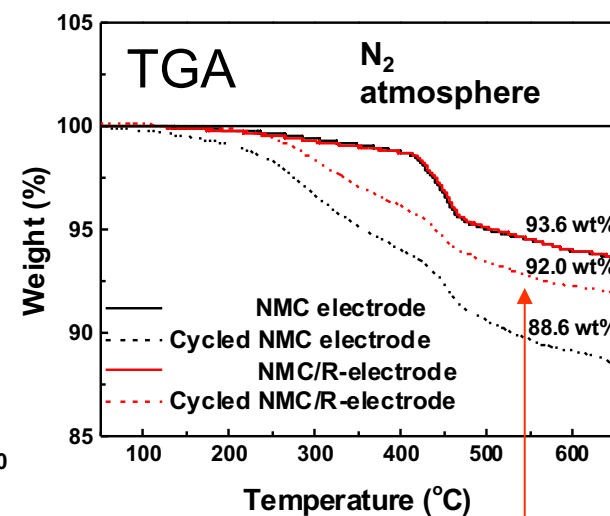
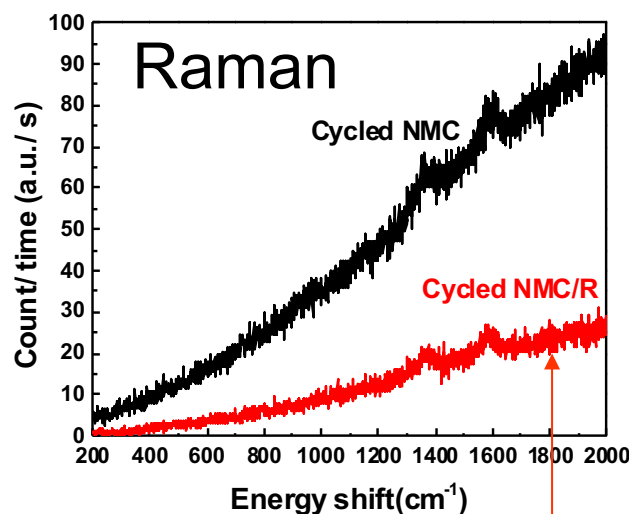
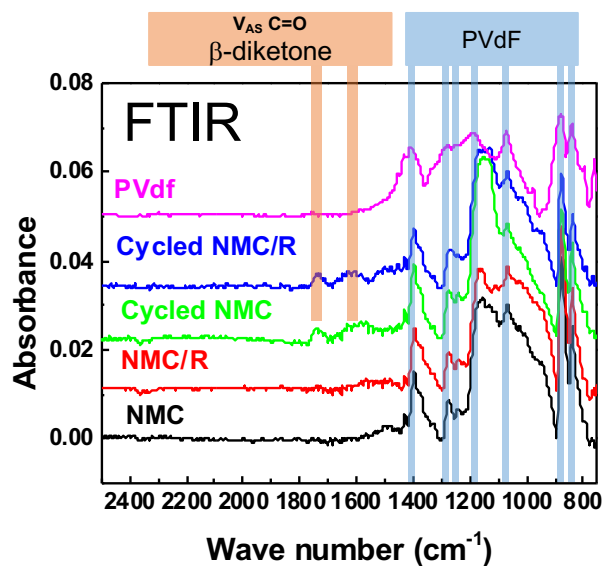
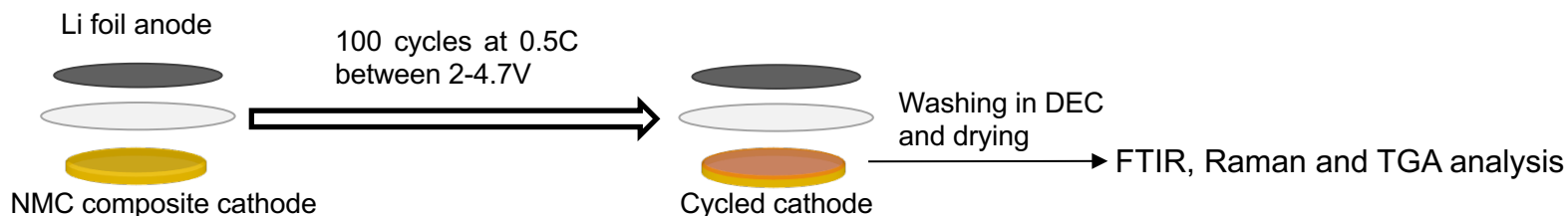


- Cycling of NMC cathodes induces (further) growth of surface reconstruction layer
- Cycled NMC/R electrodes show much less surface transition Me reduction than NMC

The artificially induced surface reconstruction layer suppresses further reduction of Me at the surface of NMC during cycling

The Effect of Surface Reconstruction in NMCs Materials

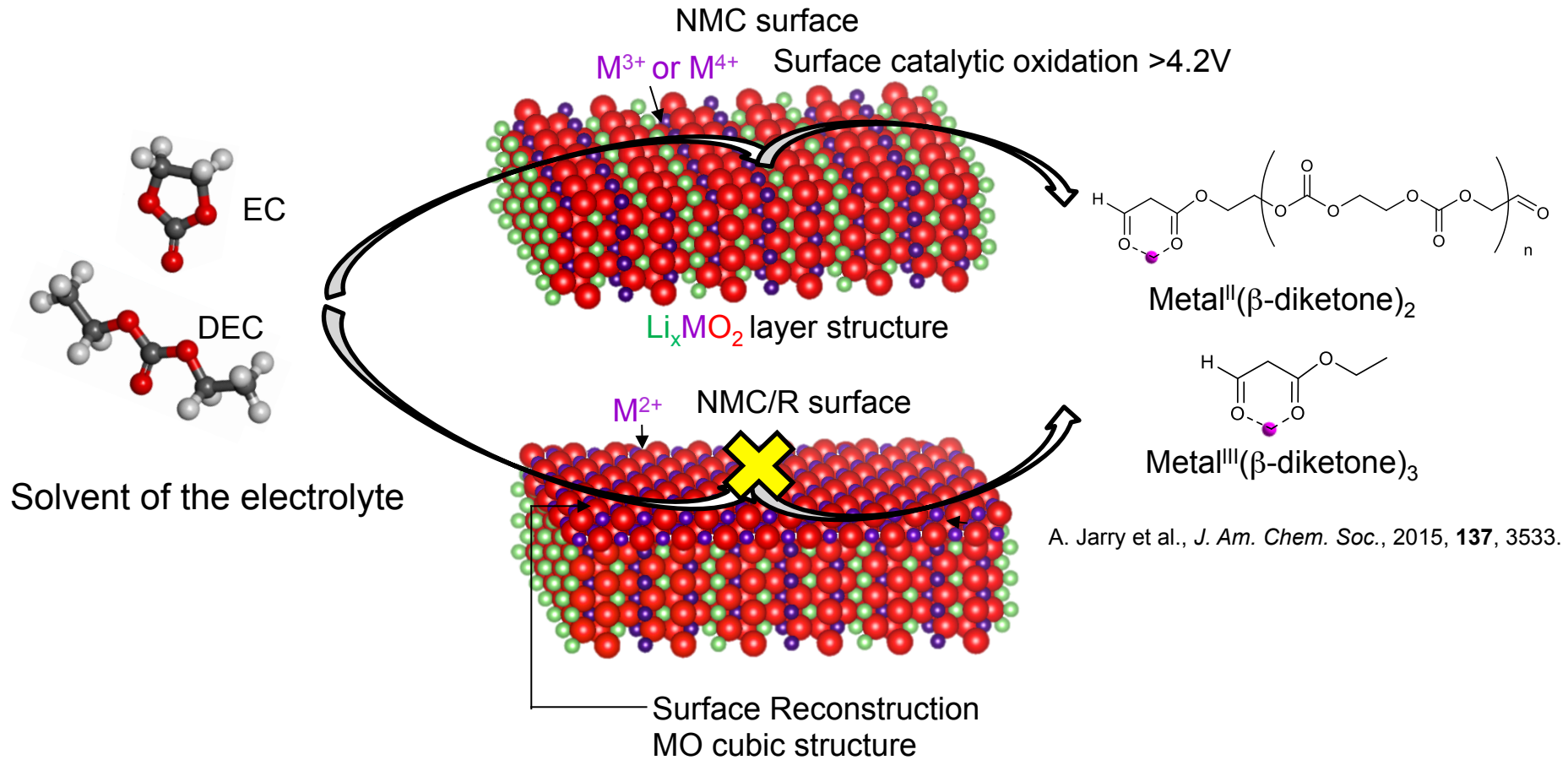
Surface Film Characterization



- Fluorescent Me (β -diketone) products form on the surface of NMC electrodes during electrochemical cycling
- Cycled NMC/R electrodes exhibit less fluorescence emission – smaller amount of electrolyte decomposition products on the surface than cycled NMC electrode

The artificially induced surface reconstruction layer inhibits formation of surface film and Me dissolution during cycling of the NMC cathode

Surface Reactivity of High-Voltage Cathodes



Surface reconstruction layer on NMC surface suppresses oxidation of EC/DEC, inhibits electrolyte oxidation, surface film formation and Me dissolution during cycling

Surface Reactivity of High-Voltage Cathodes

Summary

- Surface reconstruction layer is NOT the root cause of impedance rise and capacity fade fading of the Ni-rich NMC electrode.
 - “Pristine” NMC material and NMC with the artificially induced surface reconstruction layer exhibit similar initial electrochemical behavior.
- NMC material with the artificially induced surface reconstruction layer shows better long-term cycle performance than “pristine ”NMC”.
 - Surface reconstruction layer on NMC surface suppresses oxidation of EC/DEC, inhibits electrolyte oxidation, surface film formation and Me dissolution during cycling
- Artificially induced surface structure reconstruction can be an effective strategy of reducing NMC surface reactivity and electrode impedance growth.

This study not only determines the mechanism of surface reduced layer formation but also offer unique insight into its direct and indirect impact on the electrochemical performance and interrelated mechanism of interfacial phenomena at high-voltage cathodes.

Remaining Challenges and Barriers

1. The cathode fading mechanism must be address with impact factors for different detrimental reaction happened at different interface of the electrode.
2. The interface reaction need to be dynamic diagnosed with spatial information for studying the affective area and reaction kinetics.

Future Work

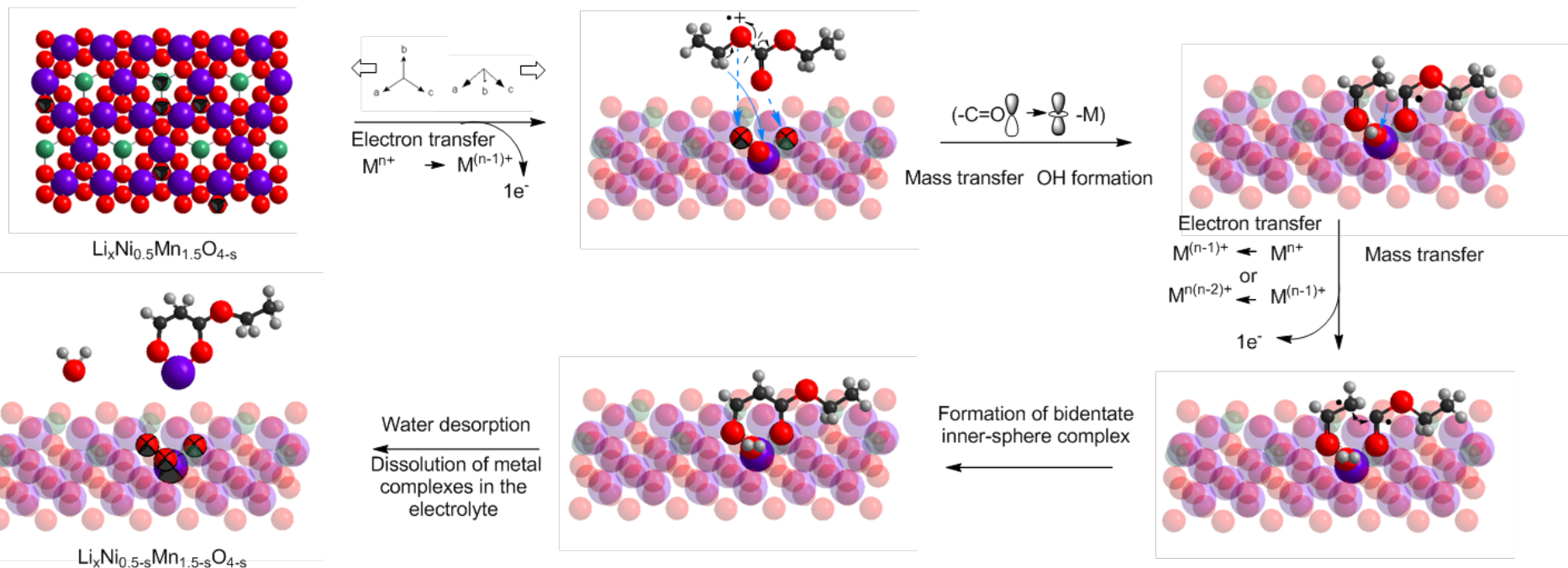
- Develop and apply advanced characterization techniques and well controlled thin film model system to obtain detailed insight into detrimental processes at electrode/electrolyte interfaces of high voltage Ni-rich NMC-type cathode materials.
- Study the crosstalk and quantify the effect of each the side reaction happened in cathode, including surface reconstruction, oxygen loss and transition metal dissolution, conductive carbon oxidation, Al current collector surface correction, and films formation at each electrolyte-solid interfaces during electrochemical cycling.
- Work closely with ABMR PIs to establish clear connections between diagnostics, theory/modelling, materials synthesis, and cell development efforts.
- Develop and apply novel innovative experimental methodologies to study and understand the basic function and mechanism of operation of materials, composite electrodes, and Li-ion cells for PHEV and EV applications.

Any proposed future work is subject to change based on funding levels.

Technical Back-Up Slides

The Mechanism of Formation of Metal Complexes at the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode. Oxidation of DEC

- Oxidation potential of DEC decreases from 5.7 to 4.2 V in the presence of PF_6^- anions and surface defects in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_{4-s}$.
- DEC oxidation occurs via two proton coupled electron transfer (PCET) associated with ligands adsorption.

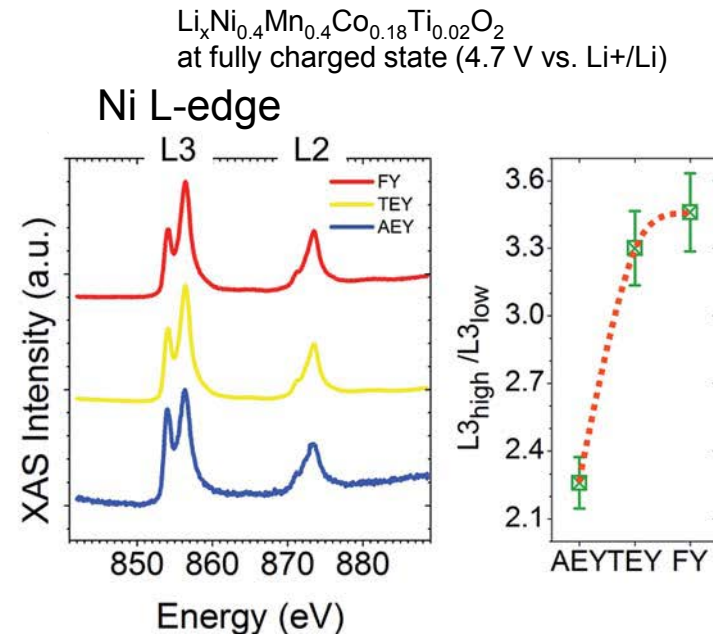
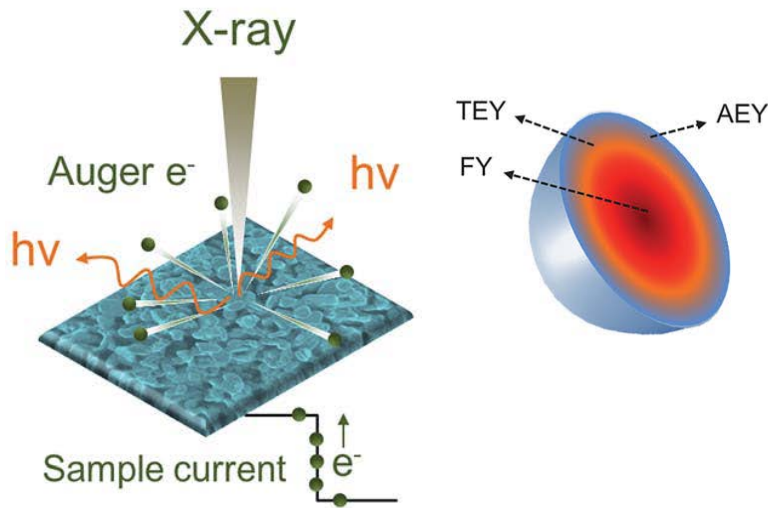


- DEC oxidation occurs preferentially at $E > 4.2$ V at Mn^{4+} surface sites.
- DEC oxidation leads to formation of $\text{Mn}(\beta\text{-diketone})$ fluorescent complexes and water.
- $\text{Mn}(\beta\text{-diketone})$ fluorescence complexes with short side chains are soluble in the electrolyte.

The X-ray Adsorption Spectrum Technique for Probing Surface Chemistry in Different Depth.

XAS can acquire chemical information from different probing depth by using three detection modes:

- Auger electron yield (AEY, 1–2 nm)
- Total electron yield (TEY, 2–5 nm)
- Fluorescence yield (FY, ~50 nm).



- TEY and AEY mode of XAS is suitable to probe the surface reconstruction layer in the order of few nano meters.
- FY mode of XAS can behave the chemical state of bulk structure.